

Enhancing Electrochemical Sensor Performance: Studies of Electrodes Tailored with ZnO/ZnFe<sub>2</sub>O<sub>4</sub> Nanoparticles

*Original*

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### Enhancing Electrochemical Sensor Performance: Studies of Electrodes Tailored with ZnO/ZnFe<sub>2</sub>O<sub>4</sub> Nanoparticles

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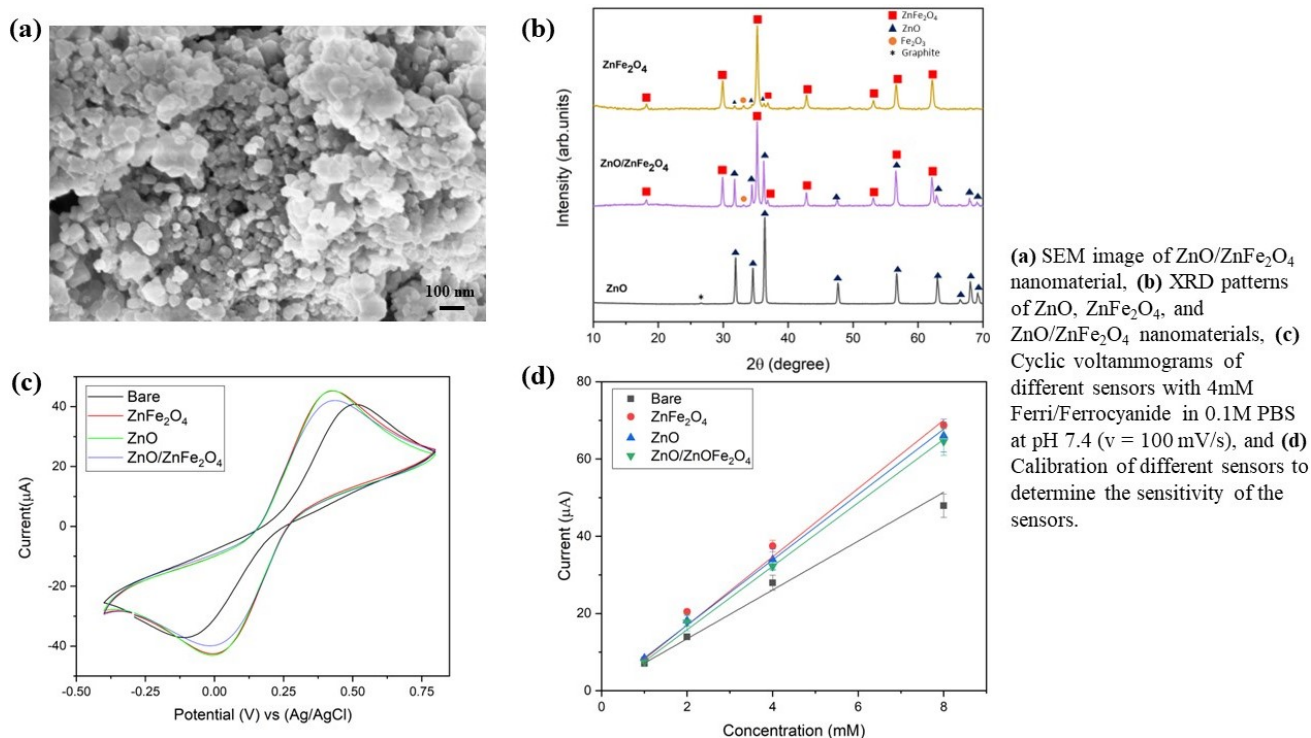
#### Abstract Text:

Spinel metal oxides possess excellent magnetic, electrical, and optical properties. They take AB<sub>2</sub>O<sub>4</sub> (face centered cubic) form with oxygen anions providing tetrahedral (Td) and octahedral (Oh) sites for A<sup>+2</sup> and B<sup>+3</sup> cations. Spinel can have a normal, inverse, or mixed form based on the occupancy of different cations in Td and Oh sites. The peculiarity of the spinel crystal structure is that its composition can be easily modified without affecting the crystal structure based on the type of cation. The type of cation in the composition defines if the spinel has a normal or inverse form [1]. Based on these premises, we have already synthesized Zn<sub>x</sub>Ni<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.2, 0.4, 0.6, 0.8, 1) nanomaterials achieving a clear gradual transition from inverse (x=0) to normal (x=1) spinel. Synthesized nanomaterials were employed as mediators in electron transfer between the screen-printed carbon working electrode and paracetamol to understand the effect of chemical composition and crystal structure on the electron transfer at the electrochemical interface [1]. Normal spinel ZnFe<sub>2</sub>O<sub>4</sub> was found to be the best nanomaterial in terms of sensitivity and kinetic rate constant. In further works, with the aim to understand the effect of ionic radii on sensitivity and electron transfer rate constant in electrochemical sensing of paracetamol, we have focused on the normal spinel structure and modified the composition by varying the concentration of Fe<sup>3+</sup> with Cr<sup>3+</sup> and Bi<sup>3+</sup> [2,3]. This study also proved that the normal spinel ZnFe<sub>2</sub>O<sub>4</sub> has the highest sensitivity and electron transfer rate constant towards paracetamol sensing.

In this work, we will present the synergic effect that can be obtained by interfacing ZnFe<sub>2</sub>O<sub>4</sub> with ZnO nanomaterials by tuning the band gap of the heterogeneous structure. The aim is to understand the effect of band gap on sensitivity and electron transfer rate constant in electrochemical sensing. ZnFe<sub>2</sub>O<sub>4</sub>, ZnO, and ZnO/ZnFe<sub>2</sub>O<sub>4</sub> nanomaterials are synthesized by a simple, single step auto combustion technique using the respective metal nitrates as precursors. Nanomaterial morphology and particles size are investigated by scanning electron microscopy. X-ray diffraction technique is employed to analyze the crystal structure and identify different phases in the newly synthesized materials. Then, commercially available screen-printed carbon electrodes with carbon working electrode and carbon counter electrodes are used for the electrochemical measurements in combination with an external double junction Ag/AgCl as a reference electrode. The synthesized nanomaterials are mixed with 1-butanol and a 5  $\mu$ L solution is used to modify the surface of the carbon working electrode to mediate the redox reactions between the carbon surface and the molecule of interest. Primarily the sensors are characterized using cyclic voltammetry with ferri/ferrocyanide redox couple as a probe molecule. Improvement in sensitivity is observed for ZnFe<sub>2</sub>O<sub>4</sub> (8.85  $\pm$  0.50  $\mu$ A/mM), ZnO (8.50  $\pm$  0.30  $\mu$ A/mM), and ZnO/ZnFe<sub>2</sub>O<sub>4</sub> (8.22  $\pm$  0.16  $\mu$ A/mM) sensors compared to the bare carbon one (6.30  $\pm$  0.40  $\mu$ A/mM). By performing cyclic voltammetry at different scan rates (v) from 25 to 125 mV/s, a good linearity of redox currents with respect to  $v^{0.5}$  is observed and redox peak positions are varying linearly with  $\ln(v)$ . Peak-to-peak separation ( $\Delta E_p$ ) is reduced for ZnO/ZnFe<sub>2</sub>O<sub>4</sub> sensors compared to the carbon one. All these results suggest a faster electron transfer at the interface when the modified electrodes are used. Laviron model is employed to calculate the electron transfer rate coefficient and constant. The rate constant for ZnFe<sub>2</sub>O<sub>4</sub> (41.8  $\pm$  2.6 ms<sup>-1</sup>), ZnO (46.0  $\pm$  4.0 ms<sup>-1</sup>), and ZnO/ZnFe<sub>2</sub>O<sub>4</sub> (33.1  $\pm$  4.5 ms<sup>-1</sup>) sensors is 3 to 5 times higher as compared to the bare carbon one (9.97  $\pm$  0.78 ms<sup>-1</sup>). We are currently studying the potential application of ZnO/ZnFe<sub>2</sub>O<sub>4</sub> nanomaterials in electrochemical sensing of small molecules relevant in biomedical field (dissolved oxygen, pH) and pharmaceutical drugs (paracetamol) to assess the potential for their use in different clinical settings.

#### References:

1. M.Madagalam et al., "Unraveling the effect of chemical and structural composition of  $Zn_xNi_{1-x}Fe_2O_4$  on the electron transfer at the electrochemical interface," *Small Struct.* 2023, 2300163.
2. M.Madagalam et al., " $ZnM_xFe_{2-x}O_4$  (M=Cr, Bi) Nanoparticles-modified electrochemical sensors: Effect on sensitivity and first-order kinetic rate constant," *2023 IEEE BioSensors Conference (BioSensors)*, London, United Kingdom, 2023, pp. 1-4, doi: 10.1109/BioSensors58001.2023.10280910.
3. M. Madagalam et al., " $ZnCr_{2-x}Fe_xO_4$  Nanoparticles-Modified Electrochemical Sensors: A Comparative Study," *2023 IEEE SENSORS*, Vienna, Austria, 2023, pp. 01-04, doi: 10.1109/SENSORS56945.2023.10325135.



(a) SEM image of ZnO/ZnFe<sub>2</sub>O<sub>4</sub> nanomaterial, (b) XRD patterns of ZnO, ZnFe<sub>2</sub>O<sub>4</sub>, and ZnO/ZnFe<sub>2</sub>O<sub>4</sub> nanomaterials, (c) Cyclic voltammograms of different sensors with 4mM Ferri/Ferrocyanide in 0.1M PBS at pH 7.4 ( $v = 100$  mV/s), and (d) Calibration of different sensors to determine the sensitivity of the sensors.

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This paper is part of a doctoral student work.

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